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Survey of Metals in Sediments Near Quonset Point, Rhode Island

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Elevated levels of silver, cadmium, cobalt, chromium, copper, iron, manganese, nickel, lead and zinc were observed in sediments collected from Narragansett Bay off Quonset Point during autumn of 1973. The probable source of the metals contamination was an electroplating facility on Quonset Point, in continuous operation from 1943 until it was closed in spring of 1973. Data on elemental composition of surficial sediments collected from various geographical locations reported by other investigators are presented and compared to those reported herein.

New England, especially the state of Rhode Island, is a major centre for the US electroplating industry. Effects

of long-term operation of a coastally-situated New England electroplating facility on metals residues in biological and non-living matrices have not yet been investigated. Accordingly, a field survey was conducted in autumn of 1973 to measure concentrations of selected metals in bottom waters, sediments, sediment interstitial waters, and benthic fauna collected from the environs of an electroplating plant, namely, the Quonset Point Naval Air Rework Facility (NARF).

The NARF is located on the former Quonset Point Naval Air Station in North Kingstown, RI (Fig. 1). With a staff of about 1500, the NARF was the primary reconstruction centre for the US Navy aircraft in the eastern United States; it operated more or less continuously from

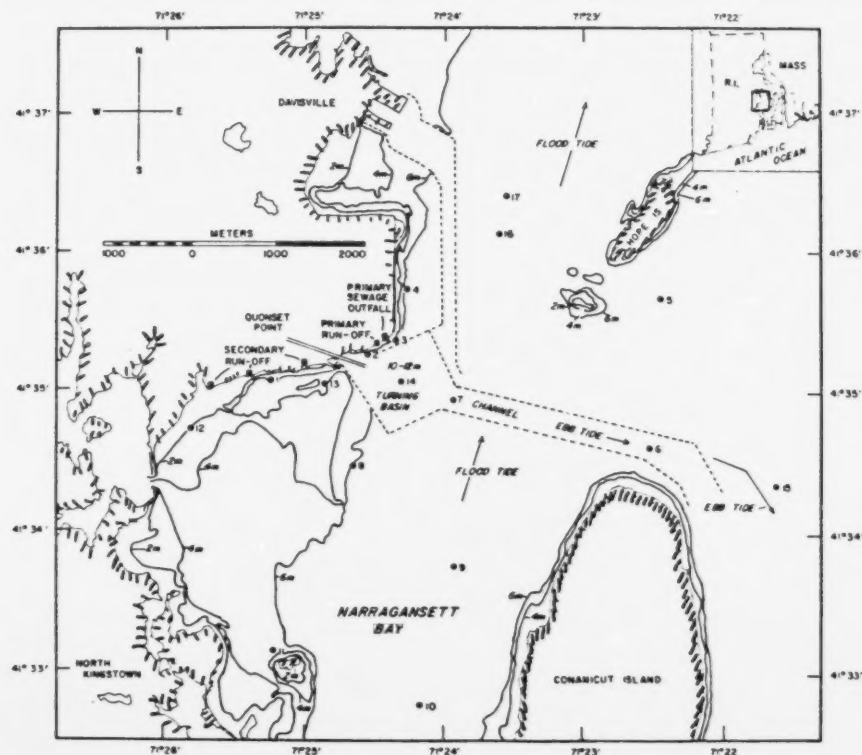


Fig. 1 Map of study area showing NARF outfalls, location of 17 sampling stations, depth contours, tidal patterns, and other features. Insert shows general location in Rhode Island.

1943 until its closure in the spring of 1973. Unfortunately, there are no reliable data on quantities or rates of metals discharged into Narragansett Bay as a result of electroplating operations. However, Air Station authorities confirmed that all wastewaters, except sewage sludge and certain caustic solutions disposed at a landfill site, were discharged eventually into Narragansett Bay through the primary sewage outfall. In addition, substantial amounts of untreated wastes from grease, paint stripping, and metal plating operations also entered the Bay through storm sewer run-off, usually during periods of heavy rain. This account is the first in a series documenting results of a survey conducted in the vicinity of the Quonset Point NARF; specifically, it reports on content of Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in sediments from nearby Narragansett Bay during October–November 1973.

Methods

Seventeen stations were selected in the study area. These were chosen on the basis of depth contours, tidal currents, distance from NARF outfalls, and channel location (Fig. 1). Four cruises were conducted (6 Sept.,

20 Sept., 12 Oct., 1 Nov.) in 1973 aboard the R/V *Billie II*. We are obliged to the Graduate School of Oceanography of the University of Rhode Island for use of the vessel. During these cruises, samples of bottom water, sediments, interstitial sediment waters, and benthic invertebrates were gathered. Sediments were collected on cruise 3 (12 Oct. 73) and 4 (1 Nov. 73). Cores up to 50 cm in length were taken by a gravity corer equipped with cellulose acetate liners. Liners were 4.5 cm internal diameter and equipped with a plastic cutting edge. Upon collection, cores were subdivided into three components: upper (0–5 cm), middle (5–15 cm), and lower (15 up to 50 cm). For each cruise a single core sample was acquired at each station. Sometimes, because of sediment composition and logistical problems, it was not possible to obtain cores in excess of 15 cm; in those cases, only upper and middle components were retained for metals analysis. Core fractions were stored in polyethylene bags on ice. In the laboratory, about 50 g from each core fraction were freeze-dried for 48 h using a Virtis freeze-mobile at a shelf temperature of -38°C , a condenser temperature of -60°C , and vacuum of less than $4\ \mu\text{m Hg}$. One g dried material was weighed from each homogenized core fraction, refluxed at 65°C in 5 ml of conc. HNO_3 for 24 h,

TABLE 1
Concentrations of 10 metals in sediment samples collected 12 Oct. 1973.
Values for upper (0–5 cm), middle (5–15 cm), and lower (15+) sediment fractions are in mg/kg dry wt except iron which is in g/kg dry wt.

Station	Fraction	Ag	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	U	0.31	0.48	0.2	13	26	6.37	68	5.6	17	53
1	M	0.77	0.62	3.2	15	21	7.34	78	6.9	19	52
2	U	2.28	3.27	4.9	76	84	18.93	155	36.6	86	156
2	M	3.41	3.92	6.0	83	122	23.02	197	35.2	89	206
2	L	1.66	3.65	4.0	34	68	15.97	133	20.2	79	139
3	U	0.58	1.00	6.6	25	28	20.59	196	20.2	16	76
3	M	0.74	0.25	5.5	22	21	18.42	163	15.6	45	67
3	L	0.47	0.08	8.8	19	25	21.59	189	16.6	14	62
4	U	1.74	0.17	7.1	55	71	20.05	191	18.8	50	122
4	M	0.49	0.66	1.2	14	14	11.54	114	8.3	12	44
5	U	1.38	0.08	7.1	68	71	28.03	339	24.8	69	153
5	M	1.25	0.25	5.9	61	56	27.03	245	20.7	51	143
5	L	0.55	0.08	9.8	34	16	29.20	243	19.8	17	75
6	U	1.43	0.08	6.7	54	50	22.69	225	20.6	54	117
6	M	0.54	0.16	6.5	34	20	22.70	233	16.6	22	72
6	L	0.49	0.17	2.6	29	9	24.55	221	15.8	12	58
7	U	1.96	0.25	3.8	68	75	26.44	242	23.9	61	153
7	M	1.58	0.33	6.3	60	70	25.22	235	20.3	47	147
7	L	1.06	0.16	4.0	48	39	26.94	231	18.2	37	120
8	U	0.99	0.25	1.9	45	51	17.57	155	15.9	38	105
8	M	0.99	0.33	4.8	42	38	18.20	174	14.8	35	109
9	U	1.58	0.25	2.8	52	60	22.54	211	21.4	49	133
9	M	0.91	0.17	7.9	43	33	19.83	165	13.7	34	104
9	L	0.31	0.16	4.0	26	12	20.81	183	14.3	12	70
10	U	1.08	0.25	3.6	43	44	23.58	193	18.4	39	125
10	M	0.66	0.00	6.0	38	27	27.41	207	15.7	30	114
11	U	1.22	0.65	3.2	36	27	18.61	209	14.5	32	104
11	M	0.49	0.41	5.8	30	14	21.39	228	13.4	16	97
11	L	0.48	0.08	3.6	28	8	22.79	233	14.6	13	62
12	U	2.85	0.40	4.1	23	26	9.67	136	7.6	25	72
12	M	2.34	0.24	1.2	22	17	10.21	143	7.4	18	69
13	U	1.91	0.83	5.8	42	49	16.43	186	14.9	45	103
13	M	0.50	0.50	3.3	24	25	14.40	146	10.0	20	72
14	U	2.50	0.33	5.5	80	93	30.12	291	24.6	75	171
14	M	2.45	0.65	7.3	81	98	29.69	263	27.3	68	171
14	L	2.12	0.74	6.8	78	100	29.06	261	24.8	58	163
15	U	1.36	0.15	6.9	60	55	25.49	249	20.6	62	126
15	M	1.00	0.17	8.1	53	36	26.25	235	18.2	49	122
15	L	0.49	0.08	7.5	33	14	22.43	235	15.8	20	59
16	U	1.00	0.25	5.7	49	55	21.24	175	17.6	38	102
16	M	0.31	0.55	8.5	36	26	27.28	225	18.7	23	82
16	L	0.46	0.31	7.0	40	27	24.96	203	17.5	27	77
17	U	0.95	0.16	2.0	32	35	13.74	112	11.8	25	72
17	M	0.39	0.08	4.8	21	21	9.52	80	8.5	16	47

TABLE 2
Concentrations of 10 metals in sediment samples collected 1 Nov. 1973.
Values for upper, middle, and lower sediment fractions are in mg/kg dry wt except for iron which is in g/kg dry wt.

Station	Fraction	Ag	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	M	2.17	0.08	2.0	14	16	6.26	54	8.4	11	40
2	U	3.27	1.63	5.6	68	100	24.00	204	30.6	77	173
2	L	1.17	1.74	3.9	38	63	19.85	162	18.7	56	144
3	U	2.12	0.73	2.0	23	36	9.73	100	9.3	39	86
3	M	0.50	0.25	8.8	22	19	21.26	190	19.1	12	72
4	U	2.41	0.75	5.6	71	101	23.47	204	24.3	66	161
4	M	0.46	0.31	4.1	9	16	7.52	64	6.7	11	45
4	L	1.41	0.91	6.5	48	66	21.50	180	17.3	43	130
5	U	1.29	0.40	9.1	62	69	23.25	222	24.5	56	138
5	M	0.66	0.33	10.1	59	40	24.86	211	21.7	50	135
5	L	0.50	0.08	9.4	41	20	26.90	225	20.1	31	81
6	U	0.31	0.07	7.9	27	13	19.89	180	14.9	15	57
6	M	0.49	0.08	7.4	27	9	21.76	193	16.6	11	50
6	L	0.33	0.08	5.9	25	10	21.53	195	16.6	13	51
7	U	1.48	0.08	5.0	62	72	24.35	219	21.9	59	143
7	M	0.66	0.08	3.8	33	26	24.02	219	17.6	23	81
7	L	1.08	0.66	4.2	50	48	23.32	199	17.5	42	133
8	U	1.33	0.74	1.3	44	62	16.17	173	13.8	44	109
8	M	1.15	0.16	2.0	48	42	19.51	184	15.6	37	106
9	U	1.08	0.33	5.4	54	58	21.25	208	21.7	44	120
9	M	0.82	0.16	6.2	42	26	18.94	182	14.2	33	97
10	U	0.50	0.00	0.2	9	14	10.09	130	6.3	15	43
10	M	1.00	0.33	4.3	21	18	12.55	113	8.4	19	67
10	L	0.33	0.33	4.8	15	13	12.19	118	9.3	12	49
11	U	0.75	0.25	4.0	37	32	16.41	149	12.2	28	90
11	M	0.57	0.00	5.3	29	19	21.08	200	17.3	14	54
11	L	0.33	0.00	2.7	26	18	20.21	189	14.7	12	47
12	U	0.49	0.41	3.2	24	21	9.00	107	7.3	17	56
12	M	1.81	0.33	0.5	25	37	10.05	132	8.6	24	60
13	U	1.00	0.42	4.0	40	46	16.00	152	15.3	33	88
13	M	0.66	0.50	1.2	23	22	13.20	158	9.9	17	55
14	U	1.91	0.42	5.7	81	96	30.98	324	28.2	77	165
14	L	1.99	0.42	6.8	65	62	28.92	258	20.4	47	142
15	U	1.08	0.00	8.3	54	49	21.77	228	17.4	54	117
15	M	0.82	0.00	8.8	53	38	22.68	187	18.6	53	115
15	L	0.50	0.33	8.3	41	20	22.72	193	15.7	38	90
16	U	0.91	0.00	9.6	46	43	21.82	181	15.4	34	97
16	M	0.41	0.08	4.8	27	11	21.75	183	14.8	15	59
17	U	1.16	0.42	3.3	47	58	17.21	145	15.6	39	99
17	M	0.50	0.17	1.8	20	23	11.91	97	9.4	13	53

and heated to near dryness at 65°C. Subsequently, an additional 5 ml conc. HNO₃ was added to each sample, filtered through acid-washed Whatman 42 paper into 50 ml volumetric flasks and diluted to volume with deionized water. Samples were analysed with a Perkin-Elmer model 403 atomic absorption spectrophotometer using procedures described in the manual accompanying the instrument.

Results

Dry weight concentrations of ten metals analysed in sediment fractions taken on 12 Oct. 73 are shown in Table 1; similar data for cores collected 1 Nov. 73 are presented in Table 2. Values for individual metals were within $\pm 4\%$ as determined from analysis of replicates from the same core fraction. Cadmium, cobalt, iron and manganese were found to be distributed uniformly throughout the sediment column while silver, chromium, copper, nickel, lead and zinc were observed to be concentrated in the surficial sediment component. This pattern was repeated for each cruise.

Concentrations of individual elements, with the possible exception of cobalt, were highest at stations located in the immediate vicinity of the Quonset Point NARF, especially those nearest the outfalls, in the ship turning basin and in the ship channel; this is clearly

depicted for surficial sediments in Fig. 2. With minor exceptions, similar distribution patterns were noted for each element in middle and in lower core fractions. It is concluded that the Quonset Point NARF was probably the major contributor of metals contaminants to sediments in the study area.

Discussion

Data reported herein on means and ranges of selected metals in NARF surficial sediments (average of 17 stations), together with similar data by others from various geographical locations are shown in Table 3. It is emphasized that strict comparisons among locations was not possible owing to probable differences in grain size of sediments, organic content, mineralogy and other factors known to have a strong influence on analytical results. Nevertheless, for each location listed, the overall rank order in metal concentrations was: Zn (most abundant), then Cr, Cu, Pb, Ni, Co, Ag and Cd, in that order. This pattern could be evaluated satisfactorily using the formula of Spearman (as quoted in Snedecor, 1955, p. 165) for rank correlation.* In every case tested

* $r_s = 1 - \frac{6 \sum d^2}{n(n^2 - 1)}$ where r_s = rank correlation coefficient (with distribution identical to that of the correlation coefficient, r , when n is equal to or greater than 8); n = number of ranks; d = difference between any two rankings.

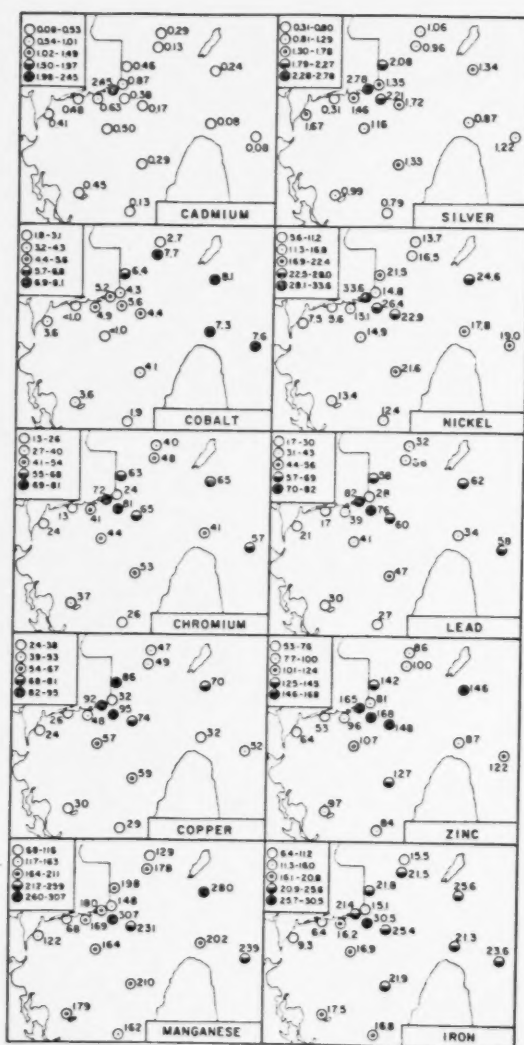


Fig. 2 Average concentrations of ten metals in surficial (0-5 cm) sediments collected in Oct-Nov 1973. All values, except those for iron, are in mg metal/kg dry wt; iron is in g/kg dry wt.

the rank order in relative abundance of metals was significant at the 0.05 probability level and lower, as determined by r_s values.

In general, highest metals concentrations in surficial sediments were observed at locations receiving anthropogenic wastes, especially sediments from the Providence River, New York Bight 'sewage site', and Narragansett Bay (this study). The actual ranking of sediments from 13 locations, as determined by r_s values, were: Providence River, which contained highest metal concentrations;

deep sea clays; New York Bight 'sewage site'; New York Bight 'dredge spoils'; shale; Narragansett Bay (this study); Fox Island, which corresponds to our station 11 in the NARF study; Rhode Island Sound 'dumpsite'; Rhode Island Sound 'controls'; New York Bight 'controls'; Philadelphia 'ocean dumpsite'; sandstone; and finally Philadelphia 'ocean controls' with lowest overall metal concentrations. This rank order held at the 0.05 probability level for all metals and locations.

From these data (Table 3) it appears that metals values

TABLE 3
Metals content of surficial sediments from various geographic locations. Values are in mg/kg dry wt, as determined by atomic absorption.

Location	Silver mean (range)	Cadmium mean (range)	Cobalt mean (range)	Chromium mean (range)	Copper mean (range)	Nickel mean (range)	Lead mean (range)	Zinc mean (range)
Narragansett Bay, RI*	1.4 (0.3-2.8)	0.47 (0.06-2.45)	4.7 (<1.0-8.1)	46 (13-81)	53 (26-98)	18 (6-34)	44 (17-81)	110 (53-168)
Providence River, RI†	15.3	4.7	7.7	428	1015	54	279	490
Fix Island, RI†	1.0	0.18	4.7	45	40	18	29	113
RI Sound 'dumpsite'†	0.7	0.50	5.0	32	30	10	17	67
Philadelphia 'ocean dumpsite'†	0.2	0.37	2.0	9	10	4	9	16
Philadelphia 'ocean controls' ‡	0.1	0.25	1.0	4	2	3	4	16
New York Bight 'controls' §	0.05	0.15	0.5	3	1	2	3	11
New York Bight 'sewage site' §				4	5	3	7	18
				102	142	23	173	252
New York Bight 'dredge spoils' §				102	(80-240)	(15-37)	(104-255)	(54-416)
					142	23	147	254
Firth of Clyde, Scotland				?	(8-395)	(3-35)	(25-372)	(25-1500)
					10	?	?	?
Gulf of Mexico, shelf ¶			5.0 (3.0-8.0)	(48-303)	10	(34-70)	(76-322)	(139-825)
				49		29	24	
Corpus Christi Bay, Texas**		?		(36-66)		(10-23)		?
		(0.05-1.95)						(10-229)
Corpus Christi Harbor, Texas**		?						?
		(2.0-130.0)						(229-11 000)
Card Sound, Florida ††		0.05			4	42	1	2
Turkey Point, Florida ††		0.33			10	25	2	5
Shale	0.07	0.35	19.0	90	45	68	20	97
Sandstone ‡‡	0.05	0.05	0.35	35	5	2	7	7
Near Shore sediments ‡‡					45	55	23	
Deep Sea Clays ‡‡		0.38	74.0	91	250	225	82	100

*This study; †Unpublished data. R. Lapan & R. Blasco, USEPA, ERL, Narragansett, personal communication; ‡Unpublished data. B. Reynolds, USEPA, ERL, Narragansett, personal communication; §Carmody *et al.* (1974); || MacKay *et al.* (1972); ¶Holmes (1973); **Holmes *et al.* (1974); ††Segar & Pellenberg (1974); ‡‡Riley & Chester (1971); Bowen (1966); Turekian & Wedepohl (1961).

for Providence River sediments especially those for Ag, Cr, and Cu are, in general, substantially higher than any other single location documented. The Providence River, which joins upper Narragansett Bay about 20 km north of the NARF, is the recipient of numerous industrial outfalls including several from electroplating plants; it is probable that the latter are the sources of observed elevated metals sediments values. The influence of Providence River wastes on sediments metals levels at stations in the NARF study area is unknown, but should not be discounted.

It is noteworthy that sediment samples from ocean depths, especially clays, contain high levels of various metals when compared to in-shore sediments. This subject area appears to merit additional research effort.

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